Supplementary Information

GC Techniques

a. Organic compound separation and analysis

Samples were analyzed by gas chromatography/mass spectrometry (GC/MS; Thermo Scientific TRACE GC Ultra gas chromatograph equipped with a Thermo Scientific DSQ II single quadrupole mass spectrometer).

Volatile organic compound analysis was carried out by introducing aqueous solution headspace into the GC/MS system by means of direct injection (1 mL by volume) using a gastight syringe. When concentration of a gaseous sample was required, SPME (Solid-phase Microextraction) fiber assembly[S1] was used. Solution analysis was mostly carried out by introducing aqueous solution samples into the GC/MS system by means of SPME. An SPME fiber assembly was suspended in the solution headspace or the solution itself for 15–20 min. Then, it was loaded into the GC inlet for 2–3 min for desorption inside the inlet. Nevertheless, when required, solution analysis was carried out by introducing aqueous solutions into the GC/MS system by means of direct injection (1 µL by volume).

For analysis of volatile organic compounds, the GC was equipped with a Q-BOND column (30 m x 0.32 mm, 10 µm film thickness). For analysis of water-soluble aldehydes and alcohols, an Rtx-200 column (30 m x 0.25 mm, 0.5 µm film thickness) was used. For the Q-BOND measurements, the oven temperature was programmed from 40 °C (held for 5 min) to 100 °C at 10 °C/min, then to 200 °C at 4 °C/min and held at the final temperature for 33 min. Helium carrier gas flow was 2.0 mL/min. For the Rtx-200 measurements, the oven temperature was programmed from 40 °C (held for 10 min) to 270 °C at 15 °C/min and held at the final temperature for 26 min. Helium carrier gas flow was 1.0 mL/min. In order to double-check the results from the above two columns, a third column was used, namely an Rxi-5ms (30 m x 0.25 mm, 0.25 µm film thickness). For the Rxi-5ms measurements, the oven temperature was programmed from 40 °C (held for 5 min) to 270 °C at 10 °C/min and held at the final temperature for 10 min. Helium carrier gas flow was 1.0 mL/min. For the three columns, transfer line temperature was 300 °C. Sample inlet port and MS source were held at 200 °C and quadrupole at room temperature.

b. H_2 separation and analysis

About 20 mg of **1** were introduced into 2 mL of thoroughly argon-degassed H_2O inside a sealed 4 mL vial. The evolved hydrogen was analyzed by injection (200 µL by volume) to a VARIAN 450-GC gas chromatograph equipped with a molecular sieve 5A packed column and a thermal conductivity detector (TCD) maintained at 170 ºC. Calibration curve or calibration point of the hydrogen peak area was made by injecting diluted mixtures of hydrogen in nitrogen. See Fig. S1 below.

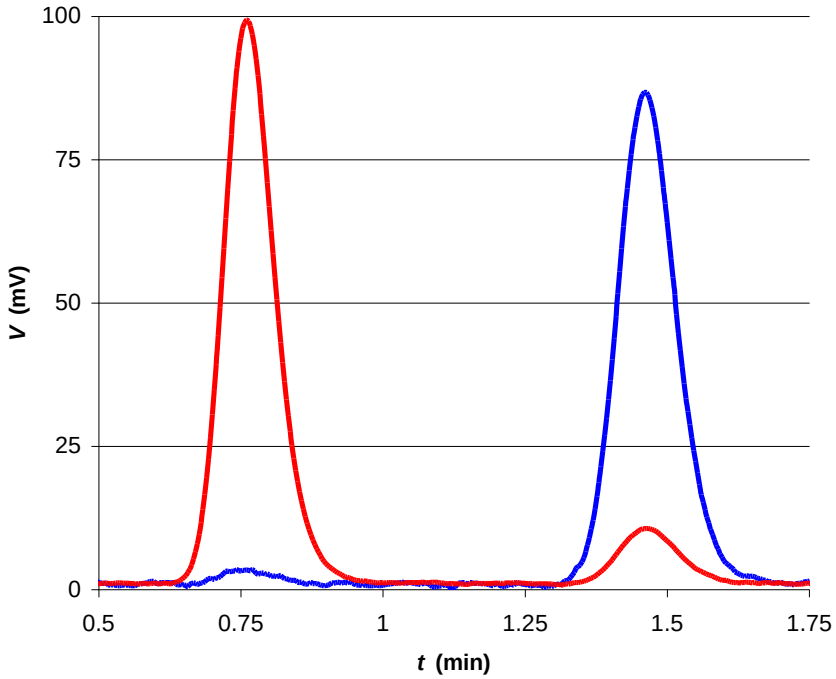

Fig. S1: Determination of H_2 in the headspace of the reaction vessel containing **1** in water. The graph contains two chromatograms (in red and blue) and shows voltage-time dependence (the output of a TCD). In each chromatogram, the left peak represents hydrogen, whereas the right one belongs to nitrogen. Calibration was performed against a standard mixture (0.17% H_2 in N_2 in red). An actual sample was collected from the vessel's headspace (0.01% H_2 in N_2 in blue).

References:

S1 Purchased from Supelco of the Sigma-Aldrich group. Product Name: SPME fiber assembly Carboxen/Polydimethylsiloxane (CAR/PDMS). Product Number: 57334-U.